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XIV. *Farther analytical experiments relative to the constitution of the prussic, of the ferruretted chyazic, and of the sulphuretted chyazic acids; and to that of their salts; together with the application of the atomic theory to the analyses of those bodies. By Robert Porrett, jun. Esq. Communicated by W. H. Wollaston, M. D. Sec. R. S.*

Read May 11, 1815.

THE Royal Society did me the honour of printing in the volume of their Transactions for last year, a paper of mine on the nature of the salts termed triple prussiates, and on acids formed by the union of certain bodies with the elements of the prussic acid.

In that paper, I endeavoured to prove, that the elements of the prussic acid would combine with a certain proportion of black oxide of iron, and form a peculiar, and hitherto unknown acid, for which I proposed the name of the ferruretted chyazic acid. I showed that this was the real acid portion of the salts which had received the erroneous appellation of triple prussiates, and that the property of combining with the prussic acid, so as to change its nature, and increase its acid properties, was not confined to the black oxide of iron, but was possessed probably by many other bodies, but certainly by sulphur, which formed with it another acid, for which I proposed the name of the sulphuretted chyazic acid. The paper also contained some analytical researches into the proportions

TABLE showing in what degree the results of my analyses coincide with the a

		Azote.	Carbon.	Hydrogen.	Prussic acid.	Red oxide of mercury.	Prussiate of mercury.	Sulphur.	Sulphuretted chyazic acid.	Pretoxide of conner.
Prussic acid.	¹ By analysis	40.7	34.8	24.5	100.	—	—	—	—	—
	per cent.	40.7047	34.8169	24.4784	100.	—	—	—	—	—
	By theory { per weight of atom.	1 atom 17.56	2 atoms 15.02	8 atoms 10.56	1 atom 43.14	—	—	—	—	—
Prussiate of mercury.	² Analysis	—	—	—	13.8	86.2	100.	—	—	—
	per cent.	—	—	—	13.7766	86.2234	100.	—	—	—
	Theory { per atom	—	—	—	1 atom 43.14	1 atom 270.	1 atom 313.14	—	—	—
Sulphuretted chyazic acid.	³ Analysis	—	—	—	34.8	—	—	65.2	100.	—
	per cent.	—	—	—	35.0333	—	—	64.9667	100.	—
	Theory { per atom.	—	—	—	1 atom 43.14	—	—	4 atoms 80.	1 atom 123.14	—
Sulphuretted chyazate of protoxide of copper.	⁴ Analysis	—	—	—	—	—	—	—	37.15	62.8
	per cent.	—	—	—	—	—	—	—	40.6215	59.3
	Theory { per atom	—	—	—	—	—	—	—	1 atom 123.14	2 atoms 180.
Sulphuretted chyazate of peroxide of copper.	⁵ Analysis	—	—	—	—	—	—	—	34.73	—
	per cent.	—	—	—	—	—	—	—	38.11	—
	Theory { per atom	—	—	—	—	—	—	—	1 atom 123.14	—
Sulphuretted chyazate of barytes.	⁶ Analysis	—	—	—	—	—	—	—	30.7	—
	per cent.	—	—	—	—	—	—	—	38.7525	—
	Theory { per atom	—	—	—	—	—	—	—	1 atom 123.14	—
Ferruretted chyazic acid.	⁷ Analysis	—	—	—	63.79	—	—	—	—	—
	per cent.	—	—	—	66.569	—	—	—	—	—
	Theory { per atom	—	—	—	4 atoms 172.56	—	—	—	—	—
Ferruretted chyazate of potash.	⁸ Analysis	—	—	—	—	—	—	—	—	—
	per cent.	—	—	—	—	—	—	—	—	—
	Theory { per atom	—	—	—	—	—	—	—	—	—
Ferruretted chyazate of black oxide of iron.	⁹ Analysis	—	—	—	—	—	—	—	—	—
	per cent.	—	—	—	—	—	—	—	—	—
	Theory { per atom	—	—	—	—	—	—	—	—	—
Ferruretted chyazate of peroxide of iron.	¹⁰ Analysis	—	—	—	—	—	—	—	—	—
	per cent.	—	—	—	—	—	—	—	—	—
	Theory { per atom	—	—	—	—	—	—	—	—	—
Ferruretted chyazate of barytes.	¹¹ Analysis	—	—	—	—	—	—	—	—	—
	per cent.	—	—	—	—	—	—	—	—	—
	Theory { per atom	—	—	—	—	—	—	—	—	—

1 Page 229 of this Paper.

2 Page 223 of this Paper.

3 Phil. Trans. for 1814, page 549, C.

4 Ditto, page 555, B.

5 Inferred from the Analysis.

6 Phil. Trans. 1814, page

[illegible]

11 Ditto, page 535.

in which the elements of these new acids are combined in them, and also into the proportions in which they unite with different saline bases.

My object in this paper, is to add to the analyses contained in the former, two analyses which I have since made; and then to apply to the whole, the admirable theory of Dalton, by which the proportions in which bodies can combine, are conceived to be governed by the relative weights of their chemical atoms, and also BERZELIUS'S addition to this theory, by which the combinations of oxides with one another, are conceived to take place in such a manner, that the oxygen contained in one of these bodies, is either equal to, or is a multiple by a whole number, of the oxygen contained in the others.

I begin with describing the two analyses to which I have just alluded.

Analysis of prussiate of mercury.

A. Fifty grains of this salt finely pulverised, were kept at the temperature of 212° for six hours, at the end of which time, they weighed exactly the same as before.

B. Forty grains of this salt were dissolved in water and decomposed by hydro-sulphuret of potash: the products of this decomposition were prussiate of potash and black sulphuret of mercury; the quantity of the former could not be ascertained with accuracy, owing to the escape of much of the prussic acid, but that of the sulphuret amounted to 37.2 grains.

C. Disappointed in my attempt to estimate the quantity of prussic acid by the last experiment, owing to its very volatile nature, I availed myself of the property I had discovered

in the hydroguretted sulphurets, of converting the prussic acid at the moment they detach it from prussiate of mercury, into sulphuretted chyazic acid; which being much less volatile, and having a stronger attraction for alkaline bases than the prussic, could not escape from the liquid, and would give me the quantity of prussic acid it represented, by deducting from its weight, that of the sulphur which I knew to exist in it. I therefore dissolved 10 grains of prussiate of mercury in hot water, and poured hydroguretted sulphuret of soda into the solution until it no longer occasioned a black precipitate. This black precipitate when dry, weighed 9.3 grains; to the liquid from which it was separated, I added a few drops of diluted sulphuric acid; these caused a separation of a minute quantity of sulphur, which was got rid of by subsidence, after which I poured into it an aqueous solution of the two sulphates of copper, and of black oxide of iron, in which the former salt was to the latter by weight, as 2 is to 3, until no farther effect was produced. By these means I threw down the whole of the sulphuretted chyazic acid contained in the liquid, and collected it combined with protoxide of copper, in the form of an insoluble white salt, which weighed 9.7 grains.

But as 100 grains of this salt contain 40.62 grains of sulphuretted chyazic acid, composed of 26.39 sulphur and 14.23 prussic acid, according to my analysis, *Phil. Tran.* for 1814, page 549, Exp. C, (corrected by calculations in the Table facing page 230 of the present paper), therefore the before mentioned 9.7 grains represent 1.38 of prussic acid, which according to this experiment is the quantity existing in 10 grains of prussiate of mercury.

D. I had next to ascertain how much red oxide of mercury was represented by the 37.2 grains of black sulphuret obtained in Experiment B, and by the 9.3 grains of the same substance obtained in Experiment C. In order to effect this, I made the following experiment: 25 grains of corrosive sublimate were dissolved in water, and decomposed by hydro-sulphuret of potash; the black sulphuret thus formed, weighed 21.5 grains, which, therefore, represents 19.94 grains of red oxide of mercury, that being the quantity contained in 25 grains of corrosive sublimate.

Then as $21.5 : 19.94 :: 37.2 : 34.48$ the quantity of red oxide in 40 prussiate of mercury,

And as $21.5 : 19.94 :: 9.3 : 8.62$ the quantity of ditto in 10 of ditto,

100 grains of prussiate of mercury are therefore composed of

Prussic acid, Experiment C.	-	-	13.8
-----------------------------	---	---	------

Red oxide of mercury, Experiment B. C. and D.			86.2
---	--	--	------

			100.0
--	--	--	-------

Analysis of prussic acid.

Being very desirous of accomplishing the analysis of this acid if possible, I considered very attentively the nature of the difficulties to be surmounted in order to effect it. The principal ones appeared to me to be the following.

1st. That of always ascertaining with precision, the quantity which is the subject of analysis.

2d. That of effecting its combustion with oxygen in such a manner, that while, on the one hand, the whole of its carbon and hydrogen should be oxygenated, so on the other, that none of its azote should undergo this process.

3d. That of determining with great accuracy, the quantity of oxygen which combines with the elements of the prussic acid during its combustion, so as after allowing for what has been expended in the formation of carbonic acid, to be able to infer with confidence, from the disappearance of the rest, the quantity of hydrogen which was contained in the acid.

The property which the prussic acid possesses of assuming the liquid form at a low temperature, and that of a gas or vapour at common temperatures, the volume of which is materially influenced by mixture with other gases, and by slight alterations of temperature and pressure; did not appear to me to be favourable to the employment of it in an uncombined form for the purpose of its analysis.

I therefore determined upon employing it in the state of condensation in which it exists in prussiate of mercury, and this determination made me undertake the analysis I have just described of that salt; of the correctness of which, having satisfied myself, I conceived that I had overcome the first difficulty.

The second and third difficulties I thought would be best surmounted by employing, for the combustion of the prussic acid, the same oxide with which it is united in the prussiate of mercury, namely, the red oxide of that metal; increasing the quantity of it by multiples of that which the salt contains, until I found that the whole of the prussic acid was decomposed.

I made a number of experiments upon this plan, the results of which proved to me that the quantities of carbonic acid and of azote gases produced, did not arrive at the maximum until five times the quantity of red oxide of mercury contained

in the prussiate had been added to it, making together six of that oxide, to one of prussic acid, and that whenever a less quantity of the oxide than this had been employed, there always existed in the gaseous products, a portion of undecomposed prussic acid. I farther observed, that in all cases the volume of azote gas obtained, was exactly equal to that of the prussic acid decomposed, that the volume of carbonic acid gas produced was invariably twice that of the azote gas liberated in the same experiment, and that the carbonic acid produced accounted for only one third of the oxygen consumed. The observance of these laws by which the decomposition was regulated, enabled me in constructing the following Table (facing page 228,) to correct the minute and unavoidable inaccuracies of experiment, by the superior accuracy to be acquired by applying to the results so obtained, the corrections necessary to make them correspond with the above-mentioned laws. It enabled me also to represent in the column denoting the measures of prussic acid gas, equal quantities by equal bulks; which, for the reasons before stated, experiment does not exactly show, and thus to render evident the true progress of its decomposition.

It may be proper before proceeding farther, to describe my mode of operating, in conducting the experiments from which the Table was compiled. This mode is similar in principle to that invented by GAY LUSSAC and THENARD in their Analysis of Animal and Vegetable substances, and improved by BERZELIUS. I am greatly indebted to these two French chemists, for the valuable information respecting this kind of analysis, which I have obtained from their *Recherches Physico-Chymiques*, and to Dr. BERZELIUS for that which I have received

from his Paper on the definite proportions in which the elements of organic nature are combined, published in Dr. THOMSON'S *Annals of Philosophy* for December last. It is to this information that I principally attribute the success which has attended the experiments of a similar nature, which I have made.

The method pursued by me, however, differs in several respects from that of either of the chemists just mentioned,

1st. In the apparatus employed, which is much more simple in my process

2dly. In the nature of the oxygenised body employed to effect the combustion.

3dly. In the method to which I had recourse, for proportioning the oxygenised to the combustible body, by making the former a multiple of that which enters into chemical union with the latter.

4thly. In decomposing a much less quantity of the combustible body at a time, than either of the above chemists.

In the present case, each of these alterations appeared to me to possess very decided advantages over the other methods. How far they may be applicable to other cases, I do not pretend to determine.

Having thus generally stated in what my process differed from former ones, I proceed to rather a more particular description of it.

I prepare the peroxide of mercury which I employ, by decomposing with pure soda, a solution of corrosive sublimate. Having weighed out the proportions of prussiate of mercury, and of the peroxide which I intend to decompose, I triturate them together in a small polished mortar of porphyry or agate

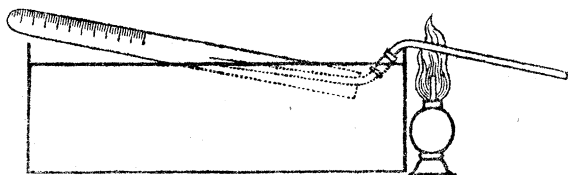
for several minutes, then collect into the centre of the mortar, what adheres to its sides, and repeat this alternate trituration and collection at least six times.

I then take a tube of glass $4\frac{1}{2}$ inches long, about the size of a common writing quill and tolerably stout, I close one end of it, and bend the other round, so that nearly an inch of that end forms a right angle with the rest. I call this the retort tube. I make a second tube similar to the first, except that instead of being closed at one end, it is open at both. I call this the adapting tube.

The retort tube is then charged with the mixed materials, by means of a small paper funnel, fixed with sealing wax to the top of the tube; the charge is introduced in about three equal portions, each of which is separated from the others by the introduction of a little coarsely powdered green glass; the charge generally occupies about $2\frac{1}{2}$ inches of the tube. After its introduction, the wax which fastened the funnel is softened by heat, and the funnel detached.

A graduated glass tube, capable of containing about $2\frac{1}{2}$ cubic inches, was next filled with mercury, and placed in the mercurial pneumatic trough, not in the usual perpendicular position, but with its upper end raised, but very little, from the horizontal situation, being about an inch above the surface of the mercury, while its lower or open end just dipped below that surface. In this position, the long leg of the adapting tube was passed up into it, which being open at both ends became filled with mercury; the short end of this tube was then connected with the short end of the retort tube, by means of a caoutchouc tube firmly tied to both. The long end of the retort tube when thus disposed, hung over the outside of

the end of the mercurial trough, in a position declining a little from the horizontal one towards the table. The decomposition was then commenced, by applying the flame of a spirit lamp to the empty part of the tube, and bringing it down gradually, so as to explode in succession the three strata of the mixture. The arrangement of the apparatus at the commencement of the process, will be instantly seen by an inspection of the annexed sketch.



When the retort tube was cold, it was separated, under the surface of the mercury, from the adapting tube, in such a manner, that any gas remaining in the latter might pass up into the graduated tube; the volume of gas collected, was then ascertained, making the necessary corrections for temperature, pressure, and the capacity of the retort tube, after which a solution of pure potash was passed up into it, and the diminution of volume which it occasioned was noticed; from the gas which remained, a deduction was made, for the quantity of atmospheric air in the upper part of the retort tube before the combustion, and which seldom exceeded $\frac{1}{30}$ of a cubic inch; the residual gas was considered as azote, and found to be so by all the tests to which I subjected it. The small quantity of solution of potash employed to effect the absorption was then examined, and if, besides carbonic acid, it was found to contain prussic acid, I concluded that I had not employed enough of the red oxide of mercury in the

TABLE showing the results of the decomposition by heat of prussiate of mercury, by i
by whole numbers of its base.

Materials before decomposition.						Products after decomposition.					
Prussiate of mercury and red oxide of mercury.						Gases.					
						Prussic acid.		Carbonic acid.		Azote.	
						Weight of oxygen in oxide of mer- cury.		Total weight of materials.			
						Grs.	Grs.	C. In.	Grs.	C. I.	Grs.
Grs.	Prussic acid.		Red. ox. merc.								
2.5 of prussiate of mercury or	0.344	+	2.155		0.159	2.5	0.395	0.2866	0.158	0.0732	0.079
Red oxy. merc.										†	0.0234
Ditto, with 2.155	-	or	0.344	+	4.31	0.319	4.655	0.316	0.2293	0.316	0.1463
Ditto, with 4.31	-	or	0.344	+	6.465	0.479	6.81	0.237	0.1719	0.474	0.2195
Ditto, with 6.465	-	or	0.344	+	8.62	0.638	8.965	0.158	0.1146	0.632	0.2926
Ditto, with 8.62	-	or	0.344	+	10.775	0.798	11.12	0.079	0.0573	0.790	0.3658
Ditto, with 10.775	-	or	0.344	+	12.93	0.957	13.275	0.000	0.0000	0.948	0.4389
										0.474	0.1401
											1.4

* Weight of carbonic acid taken as 0.463 grain for a cubic inch.

† Weight of

position by heat of prussiate of mercury, by itself, and also when mixed with multiples by whole numbers of its base.

Products after decomposition.																
Weight of oxygene in oxide of mer- cury.	Total weight of materials.	Gases.								Water.	Mercury.	Weight of oxygen in products.			Total weight of products.	
		Prussic acid.		Carbonic acid.		Azote.		Total.				In the carbonic acid.	In the water.	Total.		
		Grs.	Grs.	C. I.	Grs.	C. I.	Grs.	C. I.	Grs.							
0.159	2.5	0.395	0.2866	0.158	0.0732	0.079	0.0234	0.632	0.3832	0.1205	1.995	0.053	0.106	0.159	2.4987	
0.319	4.655	0.316	0.2293	0.316	0.1463	0.158	0.0467	0.790	0.4223	0.2410	3.991	0.106	0.213	0.319	4.6543	
0.479	6.81	0.237	0.1719	0.474	0.2195	0.237	0.0701	0.948	0.4615	0.3615	5.986	0.160	0.319	0.479	6.809	
0.638	8.965	0.158	0.1146	0.632	0.2926	0.316	0.0934	1.106	0.5006	0.4820	7.982	0.213	0.425	0.638	8.9646	
0.798	11.12	0.079	0.0573	0.790	0.3658	0.395	0.1168	1.264	0.5399	0.6025	9.977	0.266	0.532	0.798	11.1194	
0.957	13.275	0.000	0.0000	0.948	0.4389	0.474	0.1401	1.422	0.5790	0.7230	11.972	0.319	0.638	0.957	13.274	

463 grain for a cubic inch.

† Weight of azote taken as 0.2956 grain for ditto.

combustion, and repeated the experiment with an increased proportion of it.

Such was my method of effecting the analysis of the prussic acid, and by which as will be seen in the last line of the Table, I succeeded in discovering that 0.3442 gr. of it were composed as follows :

Carbon	= to that in 0.4389 gr. of carbonic acid, or 0.1198
Azote	= to the weight of the azote gas collected 0.1401
Hydrogen	= to that in 0.7230 gr. of water - 0.0843
	<hr/>
	0.3442
	<hr/>

consequently that 100 grains contain

Carbon	-	-	34.8
Azote	-	-	40.7
Hydrogen	-	-	24.5
			<hr/>
			100.0
			<hr/>

Having finished my analytical investigations, I pass on to the last divison of my subject which is the following comparative view of the composition of the prussic, ferruretted chyazic, and sulphuretted chyazic acids, and of their salts, as deduced from my analytical experiments, and as inferred from the atomic theory.

I was very well aware of the probability of my placing some of my analyses in a very unfavourable light, by contrasting the results obtained by the application of a theory, capable of giving the composition of bodies with absolute certainty, with those results which I have obtained by practical experiments, on a class of bodies hitherto little examined,

or understood, and the analyses of which were very difficult: but I would not allow this consideration to have any influence in deterring me from making such a contrast, for as I had not the vanity to give these analyses as perfect, so I feel no mortification in now proving, that they were not so; and being confident that I had not spared either time or trouble in making them, I expose their imperfections without hesitation, confiding in the candid judgment of those, who, having undertaken similar investigations, are aware of the numerous difficulties, and sources of error attendant upon them.

I have arranged and collected these comparisons into the form of a Table, which I beg leave now to introduce.

I infer from the Table, that the acids and salts included in it, are so composed as to harmonize perfectly with the doctrines of DALTON and BERZELIUS, and to be very compatible with the opinion respecting the compound nature of azote.

I shall be happy if this attempt to elucidate the nature and composition of these bodies, adds in any degree to the daily and rapid progress now making in chemical science.

ROBERT PORRETT, Jun.

Tower, Feb. 22, 1815.